

ORGANIC ELECTRODE REACTIONS: APPROACHES AND RESULTS

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The present paper does not attempt to be exhaustive, but rather to focus attention on certain trends, which seem of major importance for future studies with particular reference to unsolved problems. Consequently, only a minimum number of references are cited.

INVESTIGATIVE TECHNIQS

Developments in technics of particular relevance for the future investigation and utilization of organic electrode processes, include (1) three-electrode configurations, largely involving operational amplifier control systems, which have minimized the problems associated with the large iR drop in nonaqueous solutions, (2) reliable indicating electrodes based on graphite, which have extended the potential range available for studying electrochemical oxidations, (3) cyclic voltammetry for the identification of reversible redox couples and frequently of electroactive intermediates formed either chemically or electrolytically (recent papers on the theory of stationary electrode polarography by Shain, Nicholson, et al. (1) may provide the means for quantitatively resolving the electrochemical and associated chemical steps in electrode processes), (4) alternating current polarography and tensammetry, particularly for studying adsorption phenomena, and (5) the use of optical and magnetic resonance spectroscopic technics for identifying electrode reaction products and intermediates, e.g., (a) electron spin resonance to detect transitory free radical intermediates, (b) ellipsometry to investigate electrode surface phenomena including film formation, (c) internal reflectance technics to detect and identify electrode reaction intermediates in the solution-electrode interfacial region during electrolysis, (d) optically transparent electrodes for the concurrent examination of solutions during electrolysis by absorption spectrophotometry or internal reflectance spectroscopy, and (e) examination of luminescence phenomena which accompany the electrolytic generation of certain free radicals.

Electrolysis at controlled electrode potential, although by now a relatively old technic, is still frequently essential in preparing sufficiently large amounts of products to permit their isolation, characterization, identification and determination.

ROLE OF THE CHEMICAL ENVIRONMENT

Since it is obviously difficult to explain satisfactorily the course of many electrochemical processes unless the relevant environment is sufficiently well characterized, considerable attention has been focused on the locus of the electrode reaction (the solution-electrode interface or the electrical double layer, EDL) and on the role of the test solution composition.

The structure of the EDL and its role in electrochemical kinetics and therefore in determining the potentials of irreversible processes, which include most organic electrode reactions, are well summarized in Delahay's recent book (2). Unfortunately, in the case of organic compounds, insufficient attention is yet being given to the actual effects of adsorption on the electrode and of the potential variation

in the double layer as revealed by the extensive studies by Frumkin, Parsons, Mairanovskii and others. There is little doubt but that, in the future, the definition of the potential variation in the EDL will be a dominant factor in obtaining a more detailed picture of electrode processes. At present, there is an unfortunate tendency by some polarographers to use psi and related potentials as a deus ex machina in explaining phenomena as being due to such potentials, when their actual values either are not known or have been guessed at from other studies, which may or may not be relevant.

Related items include the increasing interest in the differentiation between surface and volume reactions, e.g., work of Mairanovskii, and the revival of interest in the correlation of electrocapillary and current-potential curves.

Nonaqueous Media. Current interest in the electrochemistry of organic compounds in nonaqueous media is due not only to the practical factors of increased solvent power and decreased solvolysis, but also to theoretical considerations, e.g., medium effects on (1) mass transport through viscosity and solvation, and (2) the potential-reaction relationship through its participation directly or via derived species in (a) the primary electrochemical reaction, (b) polarization of the reactant molecules, (c) accompanying and intermediate chemical reactions, including ion-pair formation, and (d) the structure of the EDL.

Of major importance for future work in nonaqueous media is the establishment of potential scales which will permit correlation of data obtained in aqueous and nonaqueous media. The problems involved and some possible solutions have been explored by Kolthoff (3) in a recent comprehensive paper on polarography in organic solvents. There is also a need for more careful elucidation of the reactivity of the solvent and its possible participation in electrode processes, e.g., pyridine would facilitate organic oxidations, which involve removal of protons and/or formation of carbonium ions, by acting as a proton acceptor and a carbonium ion stabilizer. Better evaluation is desirable of the purity of solvents in respect to the effect of small amounts of impurity, especially surface-active agents and water, e.g., 0.01% water in a typical solvent corresponds to a 4 or 5 mM water solution. The effect of such residual water is commonly overlooked except when the presence of a hydrogen ion source is required to complete a postulated reaction scheme.

Proton Participation. While rationalization of the experimental variation of $E_{1/2}$ with pH has been quite well done, the theories and equations derived to rationalize such behavior have not been entirely satisfactory, due primarily to (1) uncertainties in the assumptions made and in the terms used in the equations, (2) lack of specificity in respect to the physical process which the equation aims to describe, and (3) uncertainties in the experimental data (4). The nature of pH-dependent processes has been elucidated by their investigation in proton-poor solvents, coupled with the controlled addition of proton donors, e.g., phenol. A problem, which merits further investigation, is that of the role of Lewis acids in facilitating organic reduction processes.

Background Electrolyte. The effects of background electrolyte and other solution components on the observed electrochemical behavior of organic compounds are frequently quite marked and involve, among

others, the following phenomena: (1) composition, structure and potential gradient in the EDL, (2) competitive adsorption on the electrode of electroactive species, its product and other solution components, (3) activities as affected by ionic strength, equilibrium constants, etc., (4) solvation, (5) complexation, including protonation and other Lewis acid-base adduct equilibria, ion-pairing, and charge-transfer complex formation, (6) proton activity and concentrational stability, e.g., buffering, and (7) kinetics of the various equilibria listed as well as of others involving the electroactive species, e.g., its formation from a more stable solution component. Hopefully, future studies will provide more detailed models for the rationalization of electrolyte effects.

ELECTRODE REACTION MECHANISMS

Current conceptions of the mechanisms of organic electrode processes have been recently summarized by Perrin (5). Descriptions of such processes frequently still merely involve the listing of the products of the electrode reaction with, in some cases, more or less speculative postulation of intermediates formed during the reaction. Only in a few cases has there been sufficiently detailed experimental evidence to allow the postulation of structures for the transition states involved.

General Mechanistic Path. A mechanistic pattern has been outlined (6) for organic electrode processes, which not only rationalizes the general course of such processes but also the occasional changes in mechanism with experimental conditions or between members of a homologous series, e.g., reduction of a ketone to either pinacol or carbinol by selection of pH and applied potential.

The fundamental process in an organic electrochemical reduction is bond rupture, which requires only one electron to produce a free radical species; addition of a second electron completes rupture of the bond to give a carbanion. Consequently, only $1e$ or $2e$ processes need be considered in mechanism discussion; transfer of more than 2 electrons in a single polarographic wave is due to (1) mechanical fusion of waves and/or (2), more importantly, instability of the species produced as a result of the first electron-transfer step at the potential of its formation and, consequently, its immediate further reduction.

On this basis, one can postulate the general mechanism, outlined in Fig. 1, involving a generalized carbon reaction site, $R:X$, where R represents the reactive carbon center and X another carbon, oxygen, nitrogen, halogen or other atom. There may be more than one bond between R and X, e.g., in an olefinic or carbonyl group. (Electrochemical reduction is illustrated, since it has been much more extensively studied than electrochemical oxidation; generally analogous patterns can be formulated for the latter.)

In the primary step of the electrode process, the reaction site accepts a single electron to form the electrode activated complex, which can then either revert to the original species or dissociate to give a free radical precursor and an anionic species; if a multiple bond was originally present between R and X, these two species could form a single free radical anion. The exact nature of these species will be modified by the extent of participation of protons, solvent molecules and other solution constituents or even the electrode surface (participation of the latter species in subsequent steps, al-

though not explicitly indicated, may be involved.)

The free radical precursor either immediately on formation can accept a second electron and be reduced to a carbanion or can exist as a stable free radical species. The latter can either dimerize or, at more negative potential, be further reduced to the equivalent of a carbanion. The charge on the carbanion, formed by either path, can be neutralized either by acceptance of a proton from the solution or by electronic rearrangement with the charge being transferred to another part of the molecule where it can be suitably handled.

Chemical reactions preceding, accompanying or following the charge-transfer process may - and often do - play significant roles in the overall process, e.g., the possibly profound effect of the kinetics of such reactions upon the observed polarographic pattern.

The reaction scheme outlined will be illustrated by the complex pattern of five polarographic waves observed in the reduction of pyrimidine in aqueous solution. As an example of a more detailed postulation of an organic electrode process with respect to the site at which electron transfer occurs, the reduction of a ketone in acidic solution, which results in two $1e$ waves (I: pH-dependent; II: nearly pH-independent) will be considered.

Time will probably not allow discussion of (1) structure in causing steric hindrance, in the steric control of products, and in stereospecific electrode reactions, or (2) the relatively scanty measurements of heterogeneous rate constants and transfer coefficients for organic electrode reactions (cf. effect of adsorption of organic compounds on their electrochemical kinetics).

HALF-WAVE POTENTIAL CORRELATION

Correlation of polarographic $E_{1/2}$ values with numerical structural and reactivity characteristics is usually based on the postulation that the characteristic $E_{1/2}$ of a compound is a function of electron density and other factors, which, in turn, are also relatively simply related to some biological, physical or chemical property. The frequently resulting linear relationship between $E_{1/2}$ for a series of more or less closely related compounds and a suitably selected mathematical function of the values of the given property for that series of compounds permits (1) prediction of the magnitude of the property of a compound from its readily measured $E_{1/2}$ and (2) the rapid comparative evaluation of a property based on comparison of $E_{1/2}$ values.

The large variety of experimental and theoretical properties and phenomena, which have been compared to polarographically determined potential data, include photoionization potentials, degree of carcinogenesis, wavelengths of spectrophotometric absorption maxima, anti-oxidant ability, quantum mechanically calculated parameters, and structural summation characteristics. The best known and most extensively used correlations have involved various forms of the Hammett σ - ρ equation based on polar substituent quantities and the Taft modification (cf. reviews by Zuman (7) and Perrin).

Correlations of molecular orbital (M.O.) calculations with polarographic data generally involve the quantum mechanically calculated energies for adding an electron to the lowest empty M.O. or removing one from the highest occupied M.O. A priori, the optimum approach would seem to involve the use of electrochemical data based on initial

le processes, since the M.O. data apply to such processes. While such le processes can be observed for some organic compounds in aqueous media, in the case of other compounds, measurements in nonaqueous media are necessary. The validity of this approach is shown by the work of Streitwieser and others on the correlation of potentials for the oxidation of organic compounds in nonaqueous media at platinum electrodes with a variety of calculated values based on M.O. theory (cf. review by Zahradnik and Parkanyi (8)).

APPLICABILITY OF ORGANIC ELECTROCHEMISTRY

Finally, reference should be made to some applications based on the study of organic electrochemical processes, e.g., the use of polarography in elucidating problems in organic chemistry involving equilibria, rates and mechanisms, synthesis and structure.

The study of interactions is typified by Peover's work on donor-acceptor charge-transfer complexes in nonaqueous media; the formation of intermediate species was detected by polarography, which could not be picked up by spectrophotometry.

The correlation of the mechanisms of electrochemical and biological processes is a provocative possibility, which is related to the fact that electrolytic oxidations and reductions occur under experimental conditions resembling those of enzymatic and other biological transformations. Thus, the electrolytic oxidation of uric acid proceeds by a mechanism analogous to that postulated for the enzymatic oxidation.

Synthesis. The potentialities of preparative organic electrochemistry at controlled potential have, by and large, not yet been realized, being used commercially only for the small-scale production of relatively costly products. The principal limitation has been the difficulty of controlling the applied potential, which generally has to be very large because of the iR drop encountered for the appreciable current flow desirable in a preparative process.

Frequently, it is possible to control the potential by control of experimental conditions, electrolysis process and/or current drawn. An outstanding example of this approach is the work of Baizer (9), who has extensively investigated inter- and intramolecular electrolytic reductive coupling of unsaturated species to produce a variety of compounds, many of which are not readily accessible by more conventional synthesis. Adiponitrile, used in the manufacture of nylon, is now being made commercially by the electrolytic reductive coupling of acrylonitrile.

An interesting application of electrosynthesis is the generation of free radical species for study by electron spin resonance.

Fuel Cells. A considerable fraction of the research activity on fuel cells during the past decade has been focussed on the electrochemical oxidation of hydrocarbons at catalyst-type electrodes with some attention to that of oxygenated compounds, e.g., alcohols. Although there has been considerable publication of mechanistic studies, the complexity of the electrode process for the oxidation of even as simple a hydrocarbon as propane to carbon dioxide and water has defied satisfactory rationalization. The electrochemical reactions of the hydrocarbon and immediate oxidizable organic products may be masked by the electrochemical oxidation of hydrogen split off from the hydro-

carbon as active hydrogen or in a reforming reaction. The nature of the electrode is such as to favor adsorption as an essential feature of the electrochemical reaction.

Analysis. The value of polarographic and related methods for organic analysis is too well known to merit discussion except to refer to the determination of organic compounds at trace levels, e.g., the analysis of mixtures of maleic and fumaric acids at the 10^{-7} M level by the use of pulse polarography.

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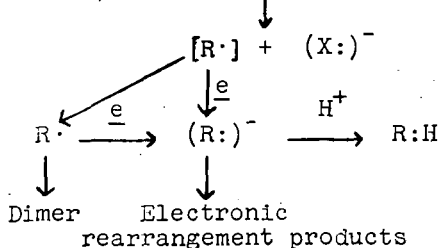
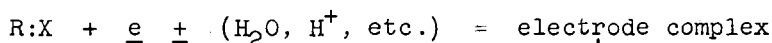


Fig. 1. Generalized reaction mechanism for an organic electrode reaction ($R:X$ represents a generalized reaction site). Allowance has to be made in the above formulation for (a) the participation of protons, solvent, other solution constituents and the electrode surface in various steps, (b) the presence of chemical reactions preceding, accompanying and following charge-transfer processes, and (c) resulting modification of the species shown.